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Letter

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Fluorescence and Phosphorescence Anisotropy from Oriented Films of Thermally Activated Delayed Fluorescence Emitters.

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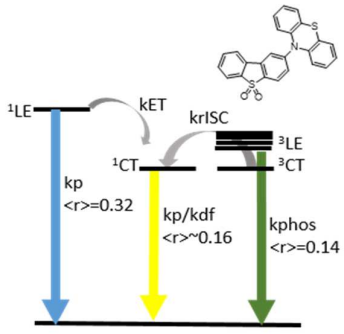
Anisotropy within three TADF materials has been observed using steady-state fluorescence polarisation. This technique has allowed for the observation of differences in polarisation within dilute solution, and both un-stretched and stretched films; the latter producing highly aligned molecules within the sample. Using these aligned films differences in anisotropy can be observed between the emission from the ^{1}LE and ^{1}CT states and upon exciting different absorption bands. Furthermore, polarisation observed from time-resolved measurements, highlights the strong vibronic coupling between charge-transfer and local triplet states.

TOC GRAPHICS



KEYWORDS Thermally-activated delayed fluorescence, polarisation, outcoupling, charge-transfer

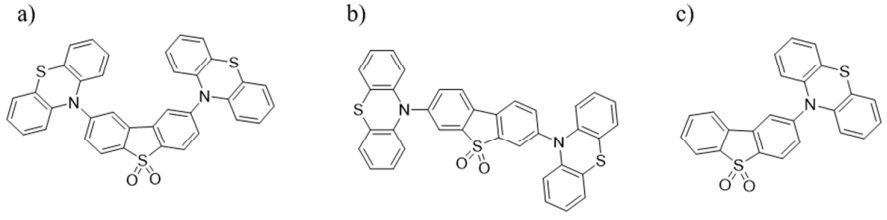
Organic light-emitting diodes (OLEDs) have come to the forefront of electronic applications due to their superior light output, colour purity and low toxicity.[1,2] Moreover, precise design of OLED materials has yielded compounds with internal quantum efficiency (IQE) of 100% without the use of expensive inorganic phosphor materials.[3,4] In many cases this has been achieved using materials capable of thermally-activated delayed fluorescence (TADF),[5-8] where fast reverse intersystem crossing (rISC) is capable of harvesting 100% of triplets back to emissive singlets.[9,10] With an abundance of OLED emitting materials exploiting TADF, a more comprehensive understanding of its mechanism is required to further knowledge of how OLED efficiency can be improved in the future.

As well as optimising the emitter for 100% efficient charge to light conversion, extracting light from a device is also a critical aspect of attaining an overall efficient OLED.[2] The process by which emission is trapped stems from how light from the emitting layer passes through further device barriers/layers of differing refractive indexes, creating total internal reflection and waveguiding within the different layers. With this in mind, the ratio of light generated internally to that which escapes the device, defines the outcoupling parameter.

Although outcoupling is often an overlooked parameter within device fabrication research, the term is of paramount importance when describing external quantum efficiency (EQE), arguably the most important parameter when determining OLED efficiency. With the fraction of light extracted limited to an estimated 20-30%, outcoupling therefore limits the EQE of a device to discouraging values.[2,11-13] The estimation of outcoupling efficiency in normal devices is based upon the assumption that within the device structure, the emitting layer contains molecules that are deposited in non-uniform orientations, creating random or isotropic emission. However research has shown that orientated emitters reduce coupling to surface plasmon modes within the interfaces of the device, increasing light extracted.[14-16]

With this knowledge in mind, there have been some investigations of molecular alignment of OLED phosphorecent[16-23] and TADF[14,24] emitters within films, using predominantly angular-dependent photoluminescence techniques in order to map the average angle of the transition dipole moment (TDM), which is fit to computational simulations. These comprehensive works, pioneered by Brütting, have shown that in some cases spontaneous horizontal molecular alignment occurs during vacuum deposition[23] therefore an investigation *via* artificial molecular alignment would prove an ideal model for studying light emission within a device structure.

Here we present an alternate technique to obtain the physical orientation of the TDM within a film; fluorescence polarisation spectroscopy. Using this experimental method, the relative angles between ground and excited state dipole moments can be determined, in order to map molecular anisotropy within three known TADF materials (Scheme 1). The results show that within mechanically stretched films, small organic emitters do align to give anisotropic emission and the absolute alignments of TDMs can be used to design better OLED emitting materials that can be deposited with enhancement of outcoupling in mind. It is therefore anticipated that comprehension of the TDM within TADF materials will help improve methods to increase outcoupling and assist quantum chemists in obtaining better models of molecular excited state properties.



Scheme 1 Structures of three TADF emitters a) 2,8-DPTZ-$DBTO_2$, b) 3,7-DPTZ-$DBTO_2$ and c) 2-PTZ-$DBTO_2$ used for anisotropy studies using fluorescence polarisation spectroscopy

The anisotropy a sample is determined *via* the following equation,

$$< r >= \frac{I_{vv} - GI_{vh}}{I_{vv} + (2GI_{vh})}, \qquad \text{-Equation 1}$$

where <r> is the anisotropy of the sample, I_{vv} denotes the intensity of light with an excitation polariser and emission polariser in the vertical position, I_{vh} denotes the intensity of light obtained with the excitation polariser in the vertical and emission polariser in the perpendicular position, and G is the instrument calibration factor, which corrects for any dependencies upon polarisation within the instrument's optical components.[25,26] Anisotropy (<r>) can be related to the angle between the absorption and emission transition dipole (θ) *via* the following,

$$< r >= \frac{2}{5} \frac{3cos^2\theta - 1}{2}, \qquad \text{-Equation 2}$$

where a <r> value of 0.4 denotes complete alignment of the absorption and emission dipole moments and -0.2 denotes a 90 ° angle between the absorption and emission dipole moments. Within stretch orientated films, alignment of the absorption dipole moment with the z-axis incident light polarisation, removes the probability of photoselection observed within isotropic materials and subsequently the 2/5 parameter from the equation. This factor however remains, due to the low symmetry of the molecules, as only in highly symmetrical molecules can $cos^2\theta$ theoretically be 1.[27]

The three molecules studied, 2,8-DPTZ-$DBTO_2$, 3,7-DPTZ-$DBTO_2$ and 2-PTZ-$DBTO_2$, were chosen for their documented TADF properties and strong charger-transfer (CT) character, (all

of which are published by our group in the literature),[9,28,29] and similar structure (Scheme 1). This structural similarity was chosen so that all changes in anisotropy could be attributed to molecular alignment and subunit conformation, rather than dipole changes due to a change in molecular structure. Absorbance of each compound in polyethylene (PE) film reproduces literature results (Figure S1), with the spectra showing a characteristic absorption band in the blue (abs_{max}~340 nm), indicative of phenothiazine absorption, and a characteristic red shifted 'tail', previously identified as direct CT absorption.[28] This indicates that the structural integrity of the compounds is preserved even after heating and casting within the PE film.

To obtain a complete picture of the anisotropy of each compound and to ensure the validity of results, the compounds were analysed in dilute (10 μM) toluene solution, in un-stretched PE film as well as oriented films containing aligned molecules, formed through mechanical stretching. Fluorescence polarisation spectroscopy of 2-PTZ-$DBTO_2$ in dilute solution shows an anisotropy close to 0, indicating, not a dipole change of 54.7 °, but the molecules' freedom to rotate on a timescale faster than the emission lifetime, resulting in emission at a large distribution of angles (Figure 1a).[30] Solution anisotropy of 2,8-DPTZ-$DBTO_2$ and 3,7-DPTZ-$DBTO_2$ show identical depolarisation effects and can be found in the supporting information (Figure S2). Depolarised emission within dilute solution is indiscriminate of emitting pathway from the excited state as both the ^{1}LE (λ_{em}~430 nm) and ^{1}CT (λ_{em}~570 nm) emission in the 3,7-DPTZ-$DBTO_2$ and 2-PTZ-$DBTO_2$ samples display an anisotropy of close to 0 across the whole emission spectrum. The result is expected due to the low viscosity of the toluene solvent and the low concentration of the solute.

Casting 2,8-DPTZ-$DBTO_2$, 3,7-DPTZ-$DBTO_2$ and 2-PTZ-$DBTO_2$ in solid PE film removes the depolarisation due to rotation seen in dilute solutions. Regardless, the un-stretched PE films also show an anisotropy of close to 0 for both ^{1}LE and ^{1}CT emission bands (Figure 1b

and S3). This means that at a concentration of 1% emitter, each molecule is randomly oriented when dispersed within the film, and thus no spontaneous alignment is found. Such depolarisation proves that the estimation of the outcoupling factor in devices using these compounds, assuming random orientation, is most likely accurate and that previously reported EQEs of more than 5% can be attributed to the increase in the charge recombination parameter (due to the presence of TADF) and not an increase in outcoupling.

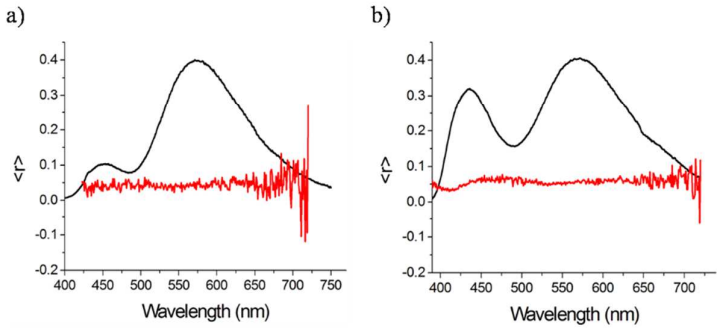


Figure 1 a) Anisotropy of 2-PTZ-DBTO$_2$ in a) a 10 μM toluene solution (red line) and b) an un-stretched PE film containing 1% w/w of the emitter (red line) (λ_{ex}370 nm). Note: The normalised emission spectrum is added in black for clarity

By stretching the film along a single axis, one can then induce molecular alignment to mimic anisotropy within an ideal OLED emissive layer. Stretched films with a stretch ratio of above 10 were analysed at different excitation wavelengths and through rotation of the film from 0-90 °; with 0 ° implying the film is placed with the stretch direction aligned with the vertically polarised excitation light, and 90 ° implying that the stretch direction is perpendicular to the vertically polarised excitation light. Upon excitation at 370 nm (into the donor phenothiazine absorption band) the stretched films emit with an anisotropy related to the film orientation (Figure 2). In the 2,8-DPTZ-DBTO$_2$ film (Figure 2a), aligned with the vertical polarisation (0 °), an anisotropy of 0.13±0.01 is observed for emission from the ^{1}CT state (at emission of 570 nm), a value denoting a difference between the absorption and emission dipole moment of 42

°. Rotation of the film within the holder to 20, 45, 60 and 90 °, the latter giving a perpendicular orientation of the stretch direction to the excitation polarisation, shows a reduction in anisotropy down to below 0. We observe an anisotropy specifically of 0 when the stretched film is oriented at the magic angle with respect to the light polarisation. This phenomenon is also observed in the 3,7-DPTZ-$DBTO_2$ and 2-PTZ-$DBTO_2$ samples. This loss in anisotropy is a direct result of film rotation, highlighting the alignment of the molecules within the sample.

For the 0 ° aligned films of 3,7-DPTZ-$DBTO_2$, an anisotropy of 0.23±0.01 at 580 nm, within the ^{1}CT emission band, is observed. This value denotes an angle between the absorption and emission dipole moments of 32 °. This difference in TDM angle between the 2,8-DPTZ-$DBTO_2$ and 3,7-DPTZ-$DBTO_2$ molecules highlights the effect of different donor positioning within the two molecules and therefore the importance of molecular configuration when designing CT emitting TADF molecules, if orientation is a target parameter. The 2-PTZ-$DBTO_2$ molecule, shows CT emission with an anisotropy of 0.18±0.01 at the emission maxima of 570 nm, showing a 37 ° angle between dipole moments. Although both 2,8-DPTZ-$DBTO_2$ and 2-PTZ-$DBTO_2$ contain donor/s placed in the same position of the acceptor, the presence of a single donor in 2-PTZ-$DBTO_2$ means that its absorption and emission must come from the same donor upon each photoexcited event, unlike 2,8-DPTZ-$DBTO_2$ which may depolarise somewhat, assuming both donors are likely to photoexcite, and may indicate different orientations of each donor.[29,31] Local excited state (^{1}LE) phenothiazine emission can also be seen in both the 2-PTZ-$DBTO_2$ and 3,7-DPTZ-$DBTO_2$ stretched films, with an anisotropy of 0.32±0.01 at the emission maxima of 430 nm in the former and 0.41±0.03 in the latter at 0 ^{o} film orientation. This highlights that within the dispersed host, there is no energy migration between emitter molecules and absorption and emission from ^{1}LE arises through the same orbitals. As excitation at 370 nm initially populates the local

excited state (^{1}LE) it is trivial to see that emission from the same ^{1}LE state (at 430 nm) should induce a smaller TDM change than emission subsequently arising from the ^{1}CT state. Furthermore, emission from both ^{1}LE and ^{1}CT states shows depolarisation upon film rotation and so it can be concluded that the ensemble of emitter molecules are all highly aligned.

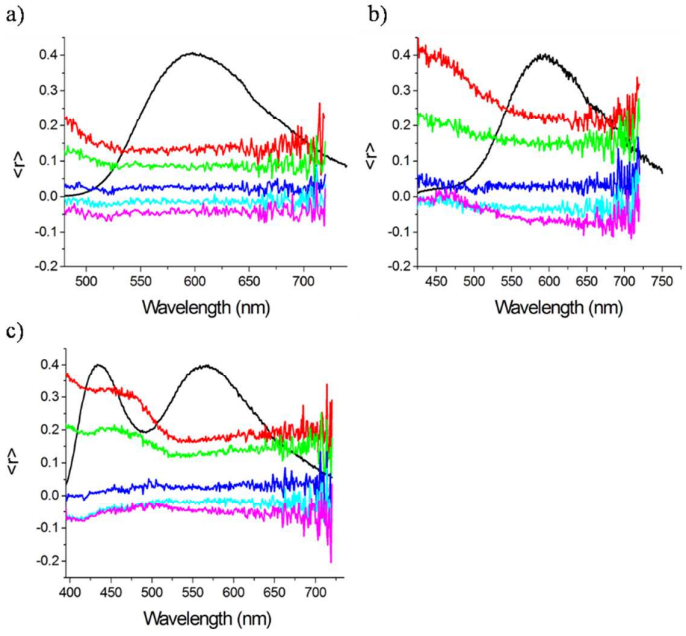


Figure 2 Anisotropy of stretched films of 1% a) 2,8-DPTZ-DBTO$_2$ b) 3,7-DPTZ-DBTO$_2$ and c) 2-PTZ-DBTO$_2$ (λ_{ex}370 nm) with the stretched film aligned at 0 ^{o} (red), 20 ^{o} (green), 45 ^{o} (blue), 60 ^{o} (cyan), and 90 ^{o} (pink). Note: The normalised emission spectrum is added in black for clarity

As well as probing anisotropy upon phenothiazine donor excitation, changes in polarisation can also be seen upon direct CT absorption. Dias *et al.* identified the presence of a direct CT absorbance band on the red edge (visible from ~ 400-470 nm) of a UV-visible spectrum of 2,8-DPTZ-DBTO$_2$ in both film and in solution.[28] To further corroborate this work, stretched films of 2,8-DPTZ-DBTO$_2$, 3,7-DPTZ-DBTO$_2$ and 2-PTZ-DBTO$_2$ were excited from 310 nm (exciting the phenothiazine donor) through to 480 nm, selectively exciting the CT absorption

band (Figure 3). Regarding 2,8-DPTZ-DBTO$_2$ with the film stretch axis aligned with the vertical polarisation, the same anisotropy of ~0.14 (for emission from the ^{1}CT state, λ_{em} 570 nm) is seen when exciting the molecule between 310-370 nm, identified as excitation of the phenothiazine ^{1}LE state (Figure 3a-red plot). Excitation between 390-480 nm produces a very significant increase in anisotropy up to 0.35±0.02, close to the maximum anisotropy and denoting a difference of only 16 ° between absorption and emission dipole moments. This alignment of absorption and emission dipoles clearly verifies this red edge absorption band as direct CT absorption.

In all three molecules, the anisotropy of the un-stretched film and the dilute solutions is not affected by the change in excitation wavelength, showing the same depolarisation in all cases. As the un-stretched film was measured in the same holder and under identical conditions as the stretched materials, it acts as an effective control for the experiment. The increase in anisotropy upon change in excitation is also seen in the 3,7-DPTZ-DBTO$_2$ molecule, displaying an anisotropy of 0.42±0.04 (when emitting from the ^{1}CT state, λ_{em} 580 nm) when excited at 480 nm, when the film is vertically aligned (Figure 3b-red plot). This value denotes complete alignment of the absorption dipole moment and the emission dipole moment, expected if attributed to the same CT state.

In all cases the anisotropy is reduced upon rotation of the film. As the film is rotated, the anisotropy diminishes to below 0, further reiterating the high degree of orientation through the stretching process. Interestingly, both the 3,7-DPTZ-DBTO$_2$ and 2-PTZ-DBTO$_2$ film, with their two distinct emission peaks, displays discrete anisotropic behaviour for both the ^{1}LE and ^{1}CT states (Figure 3c and d). In Figure 3a, b and c the presence of two absorption states (^{1}LE and ^{1}CT) is further highlighted, by monitoring the anisotropy of the CT emission as a function of excitation wavelength. In Figure 3d we show the anisotropy as a function of

excitation wavelength when monitoring the emission from the ^{1}LE (λ_{em}430 nm) state in 2-PTZ-DBTO$_2$. While excitation between 310-390 nm shows no increase in the anisotropy of the CT emission, (beginning to increase only after 390 nm-Figure 3c), we observe increasing anisotropy from the ^{1}LE emission, starting at 0.25±0.02, at 310 nm excitation, and steadily rising to 0.35±0.01 at 390 nm excitation. Assuming that the emission dipole moment of the ^{1}LE state is not changing (at a single film position), it again shows that there is more than one absorbing transition in this region which gives rise to ^{1}LE emission. Emission from the locally excited state (λ_{em}430 nm) is also affected by film rotation (due to the rotation of the aligned molecules and their emission dipole moment away from the excitation polarisation). We believe this is clear evidence of the mixing of π-π* and n-π* transitions in the absorption band tails as described by Marion[32] and in our previous work.[28,33]

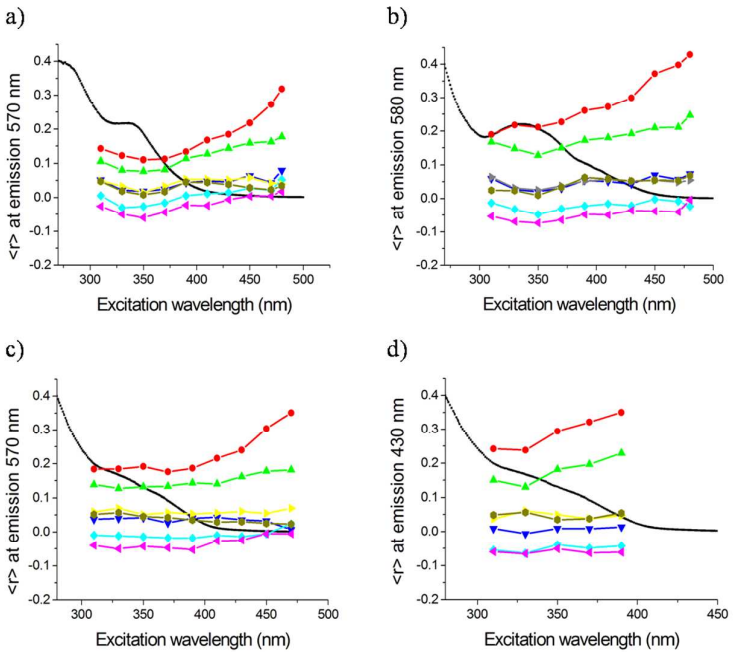


Figure 3 Anisotropy of films of 1% a) 2,8-DPTZ-DBTO$_2$ b) 3,7-DPTZ-DBTO$_2$ and c) 2-PTZ-DBTO$_2$ with emission at 570 nm or 580 nm (^{1}CT emission) d) 2-PTZ-DBTO$_2$ with emission at 430 nm (^{1}LE), at different excitation wavelengths, with the stretched film aligned

at 0 ^{o} (red), 20 ^{o} (green), 45 ^{o} (yellow), 60 ^{o} (cyan), 90 ^{o} (pink), an un-stretched film (mustard) and a 10 μM solution (blue). Note: The normalised excitation spectrum is added in black for clarity

To further characterise the position of the dipole moments within these complex molecules, we turn to time-resolved anisotropy measurements. The anisotropy of 2-PTZ-$DBTO_2$ was investigated in the nanosecond (prompt emission), early microsecond (TADF emission) and late microsecond (phosphorescence) regions, allowing for a more comprehensive picture of each TDM within this molecule (Figure S5). Polarisation was recorded using a vertically polarised Nd:YAG laser, to create a polarised excitation source, coupled with a visible polariser, placed after the sample in the set-up. As seen in the steady state measurements, a 2-PTZ-$DBTO_2$ stretched film placed parallel (0 ^{o}) to the polarised laser produces ^{1}LE emission anisotropy of 0.28±0.06 (λ_{em}=430 nm), with an onset of 2.98 eV and a CT anisotropy of 0.16±0.03 (λ_{em}=540 nm) at 2 ns time delay from the 0 time of the laser (Figure 4-blue plot). These values are similar to those seen in steady-state spectroscopy (Figure 2c) and can thus be considered as indicative of the TDM of the pure fluorescence states, ^{1}LE and ^{1}CT. At 3 μs time delay, clear delayed ^{1}CT emission is observed, already fully characterised by Ward *et. al,* and identified as TADF. At 0 ^{o} film alignment, this delayed emission has an anisotropy of 0.17±0.04, identical to the prompt ^{1}CT value within experimental error. This highlights that the dipole moment of the CT state is stationary, regardless of any excursions to the triplet state and back *via* rISC within the TADF mechanism. As seen in steady state polarisation spectroscopy, rotation of the film depolarises the anisotropic output (Figure S6).

At a delay time of 200 μs there is a blue shift in emission to an onset of 2.44 eV, identified as emission from the triplet, ^{3}LE state. Along with this hypsochromic shift in emission, manifests an additional change in anisotropy. At 0 ^{o} film alignment, the anisotropy is reduced

to 0.14±0.04, therefore showing a significant change between the dipole moment position of the ^{1}LE (found at very short timescales- λ_{em}430 nm) and the ^{3}LE state. In contrast, the phosphorescence anisotropy observed at long delay times appears similar to the anisotropy of the singlet CT emission. This result is therefore surprising but not unprecedented within literature. A study by Herbich *et. al.*, observed that some organic molecules displayed phosphorescence anisotropy close to that of the ^{1}CT state, not of the ^{1}LE state.[34] The data resulting from this literature is in line with the current model published by this group of the efficient rRISC process within TADF molecules, whereby spin-orbit coupling (SOC) between the ^{1}CT state and the ^{3}LE state (and vice versa) is mediated through ^{3}CT-^{3}LE vibronic coupling and second-order SOC.[35,36] These anisotropy results therefore clearly suggest that the presence of strong ^{3}CT-^{3}LE vibronic coupling, mixes these states, resulting in the observed equivalence of the ^{3}LE and ^{1}CT anisotropy. Therefore, this time-resolved polarisation spectroscopy technique not only further corroborates the theory of ^{3}CT-^{3}LE coupling within TADF materials but can be further used as a method for identifying good TADF materials in the future.

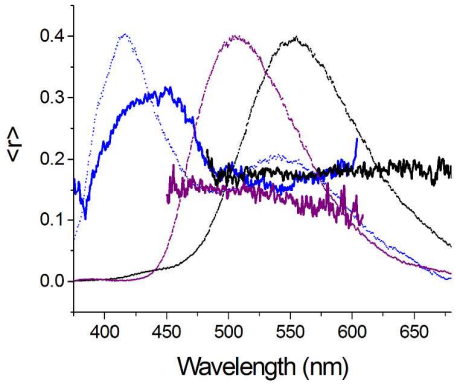


Figure 4 Time resolved anisotropy of 1% 2-PTZ-DBTO$_2$ stretched film (0 ^{o}) excited at 355 nm at 2 ns (blue), 3 μs (black), and 200 μs (purple). Note: The normalised emission spectrum (dashed lines) is added in blue (2 ns), black (3 μs) and purple (200 μs) for clarity

Polarisation spectroscopy has allowed for the identification of changes in TDM upon emission from the local and charge-transfer states. In relation to research of enhancing outcoupling, it is possible to induce TADF molecular alignment within films, allowing for the development of an accurate experimental model for dipole alignment within OLED structures, which is consistent with the observation of increased yield for outcoupled emission within devices. Nevertheless care should be taken by both experimental and computation researchers, due to the complicated excited state dynamics within these seemingly simple TADF materials. It is hoped that this and other such studies will assist quantum chemists in obtaining better models to be applied to OLED research and design.

ASSOCIATED CONTENT

Supporting Information: The Supporting Information is available free of charge on the ACS Publications website at DOI: XXXXXXXX. Provided are the experiment methods, absorbance spectra of films and additional anisotropy data.

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Notes

The authors declare no competing financial interests.

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